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The first single-molecule magnet (SMM), a dodecanuclear mixed valent manganese-oxo cluster (known as Mn_{12}-acetate) $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$,[1,2] was discovered three decades ago and changed the perspectives of how the digital information can be stored. These SMMs are molecules that show a slow relaxation of magnetization, a phenomenon that is purely molecular in origin and, unlike the bulk magnets, do not require long-range magnetic ordering. Therefore, binary storage devices that currently occupy hundreds of nanometers of space could be miniaturized to tens of Ångstroms scale. Moreover, SMMs also have potential applications in quantum computing and spintronic devices.[3,4] An important parameter for SMMs is the maximum operating temperature of an SMM, known as the blocking temperature, T_B. It is defined as the temperature below which the magnetic relaxation time (τ) is above 100 s, or as the highest temperature at which magnetic hysteresis can be observed.5 However, until recently, the blocking temperatures for these molecules always lay near absolute zero, which restricted their scope for practical use. The higher operating temperatures can be achieved by maximizing the effective activation energy for relaxation (U_{eff}) and by minimizing quantum tunnelling of magnetization (QTM) relaxation pathways. Therefore, a major focus in molecular magnetism is the design and synthesis of high-performance SMMs that suppress the QTM and show memory effects at high temperatures.

SMM research began with an era of high spin 3d metal clusters, then developed through highly anisotropic low coordinate 3d compounds, lanthanide based magnets, radical bridged compounds and 3d-4f mixed systems, among others. The current state of the art is the dysprosium metallocene, $[(Cp^{iPr5})Dy(Cp^*)]^+$, which shows an unprecedented blocking temperature of 80 K.[6] This long journey of around 30 years was a complex and multidisciplinary trajectory, involving synthetic chemists, physicists, materials scientists, and theoreticians. Each of these components is essential to understand the quantum dynamics behind these molecules. A concerted effort is needed to address the most important challenge of the field, to reduce QTM in SMM complexes, which must be overcome before the potential of these new materials can be realized in full. Therefore, the synthesis, characterization, and understanding magnetostructural correlations of the new systems are important and of interest to multidisciplinary research.

Another important class of molecules, spin crossover complexes, has been known for more than century and has become the most important class of switchable magnetic materials in recent years.[7] These molecules have two or more distinguishable electronic states, with the ability to switch between them in the presence of external stimuli like temperature, pressure, light, host:guest binding, and pH.[8] The electronic rearrangement at the metal centers causes expansion or contraction of the metal−ligand bonds and thus the lattice containing them. In turn, that is responsible for many different abrupt changes in their physical properties such as color, electrical resistance, dielectric, optical, magnetic etc.[7] Interestingly these molecules can also show multistability due to partial conversion between HS-LS states, the stability of intermediate spin states in some certain complexes or due to presence of multiple spin centers. For example, binuclear systems can adopt three molecular states (LS-LS, LS-HS, or HS-HS) which increases their potential for applications in data storage, for example. Although spin crossover is a molecular phenomenon, the nature of a spin transition (gradual, abrupt, stepwise) is highly dependent on the nature and strength of interactions between the spin centers via covalent bonds, or through weak secondary interactions. The combination of all such short- and long-range interactions is known as cooperativity. Despite establishing a suitable link between cooperativity and intermolecular interactions, the synthetic control of such forces is difficult, and knowledge of crystal engineering plays an important role. However, things become even more complicated in the presence of uncoordinated counterions and/or solvent molecules in the pores and lattices.[9] The presence of strong cooperativity in the solid state results in the abrupt transitions and wider hysteresis needed for practical application of these compounds. While SCO is most often observed in molecular crystals and coordination polymers, the complexes or nanoparticles can also be incorporated into the responsive polymers, leading to responsive soft materials for easy handling and processing.[10] This advantage has led to several applications for SCO compounds in the macroscale and nanoscale, and some very interesting molecular devices have been demonstrated in prototype.[11] Their most important feature is that in the presence of stimuli; these materials often show multiresponsive behavior. Furthermore, the switching properties often depend on particle size or the surrounding matrix.

Valence tautomeric transitions in metal complexes with redox-active ligands show some similarities to SCO systems.[12] Here also, different stimuli can be used to trigger the intramolecular electron transfer between metal and ligand, intermolecular interactions can lead to cooperativity, and it can be combined with other chemical or physical properties.

Notably, the design principles of these molecules often fail to correlate with the desired properties, and much room for understanding remains.

Therefore, this *Crystal Growth and Design* virtual special issue on Molecular Magnets and Switchable Magnetic Materials is expected to cover the latest research on molecular nano-magnets, including single-molecule magnets, single-ion magnets, single-chain magnets, relaxation mechanisms, ab initio calculations, molecular qubits, molecule-based spin devices, strong magnetic interactions, magnetic ordering, spin crossover, valence tautomerism, electron transfer, magnetocaloric materials, multifunctional magnetic materials, and novel experimental techniques for magnetic study. This virtual special issue aims to promote the understanding of magnetostructural correlation for SMM magnetic anisotropy, relaxation dynamics, valence tautomerism, and spin transition in SCO molecules and materials, that in turn directs the rational design and practical use of these materials.

References

(1) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A.-L.; Brunel, L. C.; Guillot, M. Alternating current susceptibility, high field magnetization, and millimeter band EPR evidence for a ground $S = 10$ state in $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$. *J. Am. Chem. Soc.* **1991**, *113*, 5873−5874.

(2) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. Magnetic bistability in a metal-ion cluster. *Nature* **1993**, *365*, 141.

(3) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(4) Coronado, E.; Delhaès, P.; Gatteschi, D.; Miller, J. S., Eds. *Molecular Magnetism: From Molecular Assemblies to the Devices* (NATO ASI Ser. E); Kluwer, 1995; Vol. 321.

(5) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press, 2006.

(6) Guo, F.-S.; Day, B. M.; Chen, Y.-C.; Tong, M.-L.; Mansikkamaki, A.; Layfield, R. A. Magnetic hysteresis up to 80 K in a dysprosium metallocene single-molecule magnet. *Science* **2018**, 362, 1400−1403.

(7) Halcrow, M. A. *Spin-Crossover Materials: Properties and Applications*; John Wiley & Sons, 2013.

(8) Bousseksou, A.; Molnár, G.; Salmon, L.; Nicolazzi, W. Molecular spin crossover phenomenon: recent achievements and prospects. *Chem. Soc. Rev.* **2011**, *40*, 3313−3335.

(9) Pfrunder, M. C.; Whittaker, J. J.; Parsons, S.; Moubaraki, B.; Murray, K. S.; Moggach, S. A.; Sharma, N.; Micallef, A. S.; Clegg, J. K.; McMurtrie, J. C. Controlling Spin Switching with Anionic Supramolecular Frameworks. *Chem. Mater.* **2020**, *32*, 3229−3234.

(10) Molnár, G.; Rat, S.; Salmon, L.; Nicolazzi, W.; Bousseksou, A. *Adv. Mater.* **2018**, *30*, 1703862.

(11) Senthil Kumar, K.; Ruben, M. Emerging trends in spin crossover (SCO) based functional materials and Devices Kuppusamy. *Coord. Chem. Rev.* **2017**, *346*, 176−205.

(12) Tezgerevska, T.; Alley, K. G.; Boskovic, C. Valence tautomerism in metal complexes: Stimulated and reversible intramolecular electron transfer between metal centers and organic ligands. *Coord. Chem. Rev.* **2014**, *268*, 23−40.